

1.	<p align="center">Dependence of visbroken residue viscosity and vacuum residue conversion in a commercial visbreaker unit on feedstock quality</p>
<p>Nine vacuum residual oils were characterized and eight blends of them were processed in the LUKOIL Neftohim Burgas commercial visbreaker unit. It was found that at constant content of about 8 vol.% of the fraction boiling up to 360 °C (diesel cut) in the visbroken residue the visbroken residue viscosity correlated with the vacuum residual oil visbreaker feed viscosity with a squared correlation coefficient $R^2 > 0.98$. By application of correlation analysis and intercriteria analysis the vacuum residual oil feedstock parameters which have statistically meaningful impact on conversion to products boiling below 360 °C were found to be vacuum residual oil sulfur and hydrogen content, and solubility power of maltenes. The results obtained in this work are consistent with those obtained from other groups, even for other types of vacuum residue processing like ebullated bed hydrocracking. The vacuum residual oils which contained more resinous-asphaltenic materials formed more asphaltenes in the process of thermal conversion. The vacuum residual oil viscosity increment with increasing of asphaltene content for the straight run vacuum residual oils can be described by a second order polynomial. The secondary vacuum residual oils – the visbroken vacuum residual oils exhibited a lower than straight run residual oils dependence of the residue viscosity increment on increasing of the asphaltene content.</p>	
2.	<p align="center">Investigation of relationships between petroleum properties and their impact on crude oil compatibility</p>
<p>22 crude oils around the world from which 19 processed in the LUKOIL Neftohim Burgas (LNB) refinery were characterized in the LNB research laboratory by measuring 67 properties. These 22 crude oils included light low sulfur, light sulfur, intermediate low sulfur, intermediate sulfur, intermediate high sulfur, heavy high sulfur, and extra heavy extra high sulfur crudes. A new mathematical approach – the intercriteria analysis was employed to study the relations between the petroleum properties. It was found that the petroleum properties density and sulfur content along with the crude oil simulated distillation seem to be capable of providing the same information as that from the full assay of a crude oil. Crude oils containing insoluble asphaltenes (self incompatible oils) were found to have a high content of low aromaticity naphtha and kerosene. It was found that the asphaltene solubility correlated with the asphaltene hydrogen content. The oil solubility power was found to correlate with the oil saturate content. The oil colloidal stability seems to be controlled by the rule: “like dissolves like”. The higher the aromaticity of the asphaltenes is, the higher the aromaticity of the oil is required to keep the asphaltenes in solution. The processing of blends of oils which are incompatible or nearly incompatible may deteriorate the performance of the dewatering and desalting in the refinery which consequently may damage the equipment due to accelerated corrosion, entailed by salt deposition. The processing of blends of oils which are incompatible not always can be related to an increased fouling.</p>	

3.	<p style="text-align: center;">Investigation of relationships between bulk properties and fraction properties of crude oils by application of the Intercriteria Analysis</p>
<p>Data from assays of 244 crude oils (condensates, extra light, light, intermediate, and heavy crudes) were processed by the Intercriteria analysis with the aim to investigate the relationships between bulk properties and fraction properties of the crude oils and the degree of similarity between them. It was found that except the crude bulk properties sulphur, Conradson carbon, and metals content all other studied crude bulk properties exhibited lack of statistically meaningful relations or presence of weak statistically meaningful relations with the crude fraction properties. The use of the Intercriteria analysis showed that crudes with very similar properties could be identified when a large crude data base is available. In this way based on a previous experience in oil refining a selection of potentially beneficial new crudes for processing in a refinery could be made.</p>	
4.	<p style="text-align: center;">Commercial Investigation of the Ebullated-Bed Vacuum Residue Hydrocracking in the Conversion Range of 55–93%</p>
<p>The LUKOIL Neftohim Burgas vacuum residue hydrocracking has increased the vacuum residue conversion from 55 to 93% as a result of a proper feed selection, optimal catalyst condition, and the use of a Mo nanodispersed catalyst. It was found that the feed colloidal instability index estimated from the feed saturates, aromatics, resins, and asphaltenes (SARA) data negatively correlated with the conversion. Correlations based on the use of the nonlinear least-squares method, which relates the density to the aromatic structure contents for the straight run and hydrocracked vacuum residues, were developed. Intercriteria analysis was applied to evaluate the relations between the different properties of the straight run and the hydrocracked vacuum residual oils. The density of the hydrocracked vacuum residue measured by dilution with toluene was found to strongly correlate with the conversion, Conradson carbon content, softening point, and Fraass breaking point.</p>	
5.	<p style="text-align: center;">Catalytic Cracking of Diverse Vacuum Residue Hydrocracking Gas Oils</p>
<p>10 gas oils and one deasphalted hydrocracked vacuum residue obtained from ebullated bed vacuum residue hydrocracking have been cracked in a laboratory advanced catalyst evaluation unit on a commercial fluid catalytic cracking (FCC) catalyst. It was found that the 11 secondary heavy oils obey second order reaction kinetics. The relations between gas oil properties and FCC conversion, product yields and quality were evaluated by the use of intercriteria analysis. It was found that the FCC conversion strongly correlates with the gas oil Kw-characterization factor. The product yields were established to depend on the secondary gas oil carbon atoms number, aromatic ring index, paraffinic, and aromatic carbon</p>	

content, and the total aromatics content.

6. **Role of Catalyst in Optimizing Fluid Catalytic Cracking Performance During Cracking of H-Oil-Derived Gas Oils**

Three H-Oil gas oils, heavy atmospheric gas oil (HAGO), light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGO), and two their blends with hydrotreated straight run vacuum gas oils (HTSRVGOs) were cracked on two high unit cell size (UCS) lower porosity commercial catalysts and two low UCS higher porosity commercial catalysts. The cracking experiments were performed in an advanced cracking evaluation fluid catalytic cracking (FCC) laboratory unit at 527 °C, 30 s catalyst time on stream, and catalyst-to-oil (CTO) variation between 3.5 and 7.5 wt/wt. The two high UCS lower porosity catalysts were more active and more coke selective. However, the difference between conversion of the more active high UCS lower porosity and low UCS higher porosity catalysts at 7.5 wt/wt CTO decreased in the order 10% (HAGO) > 9% (LVGO) > 6% (HVGO) > 4% (80% HTSRVGO/20% H-Oil VGO). Therefore, the catalyst performance is feedstock-dependent. The four studied catalysts along with a blend of one of them with 2% ZSM-5 were examined in a commercially revamped UOP FCC VSS unit. The lower UCS higher porosity catalysts exhibited operation at a higher CTO ratio achieving a similar conversion level with more active higher UCS lower porosity catalysts. However, the higher UCS lower porosity catalysts made 0.67% Δ coke that was higher than the maximum acceptable limit of 0.64% for this particular commercial FCC unit (FCCU), which required excluding the HVGO from the FCC feed blend. The catalyst system containing ZSM-5 increased the LPG yield but did not have an impact on gasoline octane. It was found that the predominant factor that controls refinery profitability related to the FCCU performance is the FCC slurry oil (bottoms) yield.

7. **Crude Slate, FCC slurry oil, Recycle, and Operating Conditions Effects on H-Oil® product quality**

This paper evaluates the influence of crude oil (vacuum residue) properties, the processing of fluid catalytic cracking slurry oil, and recycle of hydrocracked vacuum residue diluted with fluid catalytic cracking heavy cycle oil, and the operating conditions of the H-Oil vacuum residue hydrocracking on the quality of the H-Oil liquid products. 36 cases of operation of a commercial H-Oil® ebullated bed hydrocracker were studied at different feed composition, and different operating conditions. Intercriteria analysis was employed to define the statistically meaningful relations between 135 parameters including operating conditions, feed and products characteristics. Correlations and regression equations which related the H-Oil® mixed feed quality and the operating conditions (reaction temperature, and reaction time (throughput)) to the liquid H-Oil® products quality were developed. The developed equations can be used to find the optimal performance of the whole refinery considering that the H-Oil liquid products are part of the feed for the units: fluid catalytic cracking, hydrotreating, road

pavement bitumen, and blending.

8. **Evaluation of the different compatibility indices to model and predict oil colloidal stability and its relation to crude oil desalting**

Thirty crude oils, belonging to light, medium, heavy, and extra heavy, light sulphur, and high sulphur have been characterized and compatibility indices defined. Nine crude oil compatibility indices have been employed to evaluate the compatibility of crude blends from the thirty individual crude oils. Intercriteria analysis revealed the relations between the different compatibility indices, and the different petroleum properties. Tetra-plot was employed to model crude blend compatibility. The ratio of solubility blending number to insolubility number was found to best describe the desalting efficiency, and therefore could be considered as the compatible in-dex that best model the crude oil blend compatibility. Density of crude oil and the n-heptane dilution test seem to be sufficient to model, and predict the compatibility of crude blends.

9. **Empirical Models to Characterize the structural and physio-chemical properties of Vacuum Gas Oils with different saturate contents**

Intercriteria analysis was employed in VGO samples having a saturate content between 0.8 and 93.1 wt.% to define the statistically significant relations between physicochemical properties, empirical structural models and vacuum gas oil compositional information. The use of a logistic function and employment of a non-linear least squares method along with the aromatic ring index allowed for our newly developed correlation to accurately predict the saturate content of VGOs.. The empirical models developed in this study can be used not only for obtaining the valuable structural information necessary to predict the behavior of VGOs in the conversion processes but can also be utilized to detect incorrectly performed SARA analyses. This work confirms the possibility of predicting the contents of VGO compounds from physicochemical properties and empirical models.

10. **Comparison of Empirical Models to Predict Viscosity of Secondary Vacuum Gas Oils**

This work presents characterization data and viscosity of thirty-four secondary vacuum gas oils (H-Oil gas oils, visbreaker gas oils, and fluid catalytic cracking slurry oils) with aromatic content reaching up to 100 wt.%. Intercriteria analysis was employed to define the secondary VGO characteristic parameters which have effect on viscosity. Seven published empirical models to predict viscosity of the secondary vacuum gas oils were examined for their prediction ability. The empirical model of Aboul-Seud and Moharam was found to have the

lowest error of prediction. A modification of Aboul-Seoud and Moharam model by separating the power terms accounting for the effects of specific gravity and average boiling point improves the accuracy of viscosity prediction. It was discovered that the relation of slope of viscosity decrease with temperature enhancement for the secondary vacuum gas oil is not a constant. This slope increases with the average boiling point and the specific gravity augmentation, a fact that has not been discussed before.

11. **Different Nonlinear Regression Techniques and Sensitivity Analysis as Tools to Optimize Oil Viscosity Modeling**

Four nonlinear regression techniques were explored to model gas oil viscosity on the base of Walther's empirical equation. With the initial data base of 41 primary and secondary vacuum gas oils four models were developed with a comparable accuracy of viscosity calculation. The Akaike information criterion, and Bayesian information criterion selected the least square relative errors (LSRE) model as the best one. The sensitivity analysis with respect to given data also revealed that the LSRE model is the most stable one with the lowest values of standard deviations of derivatives. A verification of the gas oil viscosity prediction ability was done with another set of 43 gas oils showing remarkably better accuracy of LSRE model. The LSRE was also found to predict better viscosity for the 43 test gas oils relative to the Aboul Seoud and Moharam model and the Kotzakoulakis and George.

12. **Modelling the Process of Production of Diesel Fuels by the Use of Generalized Nets**

The process of commodity diesel fuel production in a refinery has been modelled by the use of the Generalized Net (GN) apparatus. GNs are extensions of Petri nets and of all their modifications and extensions. The model accounts for the orders of different grades of diesel fuel and the available amounts of the different diesel fuel components. It can be used for the synchronization and optimization of these processes.

13. **Investigation on feasibility to predict the content of saturate plus mono-nuclear aromatic hydrocarbons in vacuum gas oils from bulk properties and empirical correlations**

This work presents a study on feasibility to predict saturates plus mono-nuclear aromatic hydrocarbons content in vacuum gas oils from readily available physical properties and the empirical methods: n-d-M, API, Total, Conoco Phillips (COP), and that of Goosens. As a result of a wide literature search 44 vacuum gas oils (VGO) having saturate plus mono-nuclear aromatic hydrocarbons in the range 13.7–97.0% and specific gravity (SG) in the range 0.8648–1.0903 were selected. Based on the physical properties SG and T50 boiling point of

the 44 VGOs and the aromatic carbon and hydrogen content predicted by the Conoco-Phillips method a new correlation that predicts VGO saturate plus mono-nuclear aromatic hydrocarbons content with a reasonable accuracy was developed. This correlation based on a wide variation in properties of VGO can be used for a daily optimization of operation of FCC and hydrocracking units.

14. **Reactivity and stability of vacuum residual oils in their thermal conversion**

Thirteen vacuum residual oils originating from Russia, Middle East, Asia, and South America were thermally cracked in a modified high-temperature-high-pressure batch autoclave reactor. It was found that the colloidal stability of the vacuum residual oils expressed by S-value was the dominant factor that affected the residue thermal reactivity. SARA analysis data of the residual oils were confirmed to contain insufficient information about residue thermal reactivity and colloidal stability. It was found that the higher the colloidal stability of a residual oil the lower residue thermal reactivity and the steeper colloidal stability reduction during thermal conversion. The asphaltene solubility was found to linearly decrease with the increase of the thermal conversion, while the maltene solubility power did not always decrease with the increase of the thermal conversion for the studied residual oils. Having in mind that the ebullated bed residue hydrocracking H-Oil process is also based on thermal conversion the properties of commercial straight run Urals vacuum residue (UVR), visbreaker residue obtained by thermal cracking of UVR (UVBR), and ebullated bed hydrocracking (H-Oil) unconverted residue were investigated. It was found that asphaltene solubility lowered linearly with increasing of conversion regardless of the process: visbreaking

or ebullated bed hydrocracking. The maltene fraction average molecular weight seems to decrease with the increase of the residue thermal conversion processes visbreaking and ebullated hydrocracking as the asphaltene average molecular weight does for the same processes. It was found that the atmospheric gas oil fraction from visbreaker has no negative effect on residual oil colloidal stability while the vacuum gas oil fraction has negative impact on residue stability in both visbreaker and H-Oil unconverted residual oils. The data generated in this work study suggest that the asphaltene solubility has a bigger impact on the residual oil colloidal stability than the maltene solubility power.

15. **Cold flow properties and oxidation stability of blends of near zero sulfur diesel from Ural crude oil and FAME from different origin**

Cold flow properties and oxidation stability of near zero sulfur diesel from Ural crude oil and fatty methyl esters (FAME) from different origin and their blends were studied in this work. It was found that undercutting the petroleum diesel to obtain arctic diesel deteriorates its oxidation stability and anti-oxidant addition is required to keep the oxidation stability within acceptable limits. The addition of commercially available FAMEs, produced from 100% rape seed oil; 70% soya and 30% palm oil; 50% rape seed oil and 50% sunflower oil, to the petroleum diesel depresses the cold filter plugging point (CFPP). The depressing effect on the

conventional diesel CFPP of the FAME depends on the petroleum diesel and the FAME properties. The Honeywell software RPMS model used to predict cloud points (CP) of blends of different conventional middle distillates was found to be capable of predicting cloud points of blends of petroleum diesel and FAME. The highest class 4 of arctic diesel according to EN 590 (CP = -34 °C; CFPP = -44 °C) can be produced by blending petroleum diesel with the 100% rape seed FAME treated with cold flow improver in concentration up to 10%. The addition of the synthetic anti-oxidant ionol (BHT) to petroleum diesel with high unsaturated hydrocarbon level and to the blends petroleum diesel/FAME seems to inhibit the secondary reactions of peroxides decomposition to acids to a greater extent than the oxidative polymerization.

16. **Assessment of shelf life of Bulgarian industrial FAME by the use of modified ASTM D2274 as accelerated oxidation method**

Kinetic data for hydroperoxide formation in a commercial biodiesel, produced from 50% sunflower oil and 50% rapeseed oil were obtained by using rapid, higher than standard temperature procedure with sufficient oxygen solubility in the samples. Three different mathematical methods for processing the data and shelf life determination of the studied biodiesel are compared. The applicable methodologies are hydroperoxide concentration abrupt increase graphical determination and Q rule. The calculation shows that shelf life of the studied stabilized Bulgarian biodiesel amounts between 1.17 and 1.27 years. It was also found that peroxide value for induction period at 15 °C is 71.8 meq O₂/kg biodiesel.

17. **Industrial investigation on feasibility to raise near zero sulfur diesel production by increasing fluid catalytic cracking light cycle oil production**

Evaluation of opportunity to raise Euro V diesel production by increasing fluid catalytic cracking (FCC) light cycle oil (LCO) production was carried at the Lukoil Neftochim Bourgas, Bulgaria (LNB) refinery. The FCC LCO (IBP=360 °C) production was investigated in the FCC conversion range between 69 and 83 wt.% and LCO initial boiling point (IBP) between 177 and 210 °C. It was found that the LCO yield increased from 16.0 up to 20.7 wt.% by decreasing conversion from 83 to 69 wt.%. At constant conversion in the FCC unit of 79.7 wt.% the LCO yield increased from 17.8 to 24.8 wt.% by decreasing the IBP from 210 to 177 °C. A further 3.5 wt.% LCO yield increase and meeting the diesel flash point specification of 55 °C can be achieved by lowering the LCO IBP down to 163 °C. It was found that during hydrotreatment of a blend of the LNB middle distillates and LCO in a high pressure (70 bars) hydrotreater employing Co-Mo catalyst the maximum LCO (IBP=210;FBP=300 °C) content that allows meeting the EN specifications is 10 wt.%. If the LCO IBP is reduced to 177 °C then the maximum LCO content in the feed can reach 20 wt.%. The limitation of density not higher than 0.845 g/cm³ in the hydrotreated product at 15 °C is the restriction for further increase of LCO content in hydrotreater feed. Replacing the Co-Mo catalyst by Ni-Mo and noble metal catalysts in the high pressure hydrotreater can allow more

than double increase of LCO content in hydrotreater feed. Hydrogen chemical consumption in that case, however is also more than twofold.

18. **Fluid catalytic cracking feed hydrotreatment and its severity impact on product yields and quality**

This paper investigates the effect of fluid catalytic cracking (FCC) feed hydrotreatment and its severity increase on product yields and quality obtained in a commercial and a laboratory MAT FCC units. The hydrotreatment of Ural heavy vacuum gas oil reduces not only sulfur, nitrogen, Conradson carbon and metals content in the FCC feed but also increases the mononuclear aromatic hydrocarbons content by 8% absolute at almost no change in the total aromatics content. Regardless of this 8% increase of the mononuclear aromatics in the hydrotreated FCC feed the conversion increase in both commercial and laboratory MAT units was only 2%. The severity increase in the FCC feed hydrotreater leads to a higher conversion in the FCC, higher hydrogen transfer rate that results in higher isobutane/butylenes ratio, lower gasoline olefins content, and higher gasoline motor octane number. The hydrotreatment of the Ural heavy vacuum gas oil exhibited the same changes in FCC catalyst selectivities: lower coke and LCO selectivities and higher gasoline selectivity in both commercial riser FCC unit that has between 2 and 3 s time on stream, and the fixed bed reactor MAT unit, that has 30 s time on stream.

19. **Opportunity to Improve Diesel-Fuel Cetane-Number Prediction from Easily Available Physical Properties and Application of the Least-Squares Method and Artificial Neural Networks**

A database of 140 diesel fuels having cetane numbers in the range of 10–70 points; densities at 15 °C; and distillation characteristics according to ASTM D-86 T10%, T50%, and T90% was used to develop new procedures for predicting diesel cetane numbers by application of the least-squares method (LSM) using MAPLE software and an artificial neural network (ANN) using MATLAB. The existing standard methods of determining cetane-index values, ASTM D-976 and ASTM D-4737, which are correlations of the cetane number, confirmed the earlier conclusions that these methods predict the cetane number with a large variation. The four-variable ASTM D-4737 method was found to better approximate the diesel cetane number than the two-variable ASTM D-976 method. The developed four cetane-index models (one LSM and three ANN models) were found to better approximate the middle-distillate cetane numbers. Between 4% and 5% of the selected database of 140 middle distillates were samples with differences between their measured cetane numbers and the cetane-index values predicted by the four new procedures was higher than the specified reproducibility limit in the standard for measuring cetane number, ASTM D-613. In contrast, the cetane-index values calculated in accordance with standards ASTM D-976 and ASTM D-4737 demonstrated that 18% and 16% of the selected database of 140 middle distillates, respectively, were samples

with differences between their measured cetane numbers and predicted cetane-index values higher than the specified reproducibility limit in standard ASTM D-613. The ASTM D-4737 method, LSM, and three ANN models were tested against 22 middle distillates not included in the database of 140 diesel fuels. The LSM cetane index showed the best cetane-number prediction capability among all of the models tested.

20. **Investigation on sediment formation in residue thermal conversion based processes**

The thermal conversion of fifteen vacuum residual oils (VROs) having different properties was investigated in a modified high-temperature–high-pressure batch autoclave reactor. It was found that the sediment level (toluene insoluble) in the unconverted residual oil demonstrated a behavior typical for presence of induction period. The sediment level at the end of the induction period was mostly influenced by feedstock colloidal stability. The rate of sediment formation after the induction period was mostly influenced by VRO resin content. The results in this study do not support the assumption that the more aromatic VROs generate more coke-like sediments during thermal conversion. The higher density and aromatic VROs generated less sediment. The addition of high aromatic fluid catalytic cracking (FCC) slurry oil to a VRO decreased the thermal reactor surface deposit. The effect of this coke-like reactor sediment reduction is attributed to improvement in VRO asphaltene solubility by the high aromatic FCC slurry oil and a possible hydrogen donating properties of this gas oil. The use of a synthetic dispersant was found to improve the asphaltene solubility limit and extend the period of conversion without forming coke-like deposit in the thermal cracking reactor. The FCC slurry demonstrated a stronger inhibition effect on sediment formation than the synthetic dispersant probably because it is a stronger solvent and/or because it possesses hydrogen donating properties.

21. **Study on the origin of sediment formation in a high pressure near zero sulfur diesel hydrotreater**

Lukoil Neftohim Burgas (LNB), the single refinery currently operating in Bulgaria, constructed and put into operation a new high pressure diesel hydrotreater in 2010. Since its start-up, the unit has operated smoothly by hydrotreating a heavy diesel fraction (200–360 °C) with sulfur content of 0.8% and density at 20 °C of 0.860 g/cm³ and producing hydrotreated diesel with sulfur content of 6 ppm and density at 20 °C of 0.847 g/cm³. However, in 2013 a sudden increase of the pressure of the treating gas compressor at the hydrotreater scheme was registered and the unit had to be switched off in emergency. Sediments formed in the tubes of the heat-exchanger, used for heat transfer between the hydrotreater product and hydrogen treating gases, were found. This study presents the results from the determination of the composition and the origin of the deposit, as well as the technological solutions to prevent its formation. According of the data from different analytical techniques applied, the following composition of the deposit was supposed: 46.6% ammonium chloride, 9.6% nitrates, 13.6% organic chlorides and about 30% water, organic impurities (carbonic acids and naphthenic

hydrocarbons) and corrosion products. Numerical investigation of the temperature field in the area of the deposits is also presented.

22. Investigation of relations between properties of vacuum residual oils from different origin, and of their deasphalted and asphaltene fractions

36 vacuum residual oils, obtained from all available groups of crude oils in the world along with their deasphalted oils and their asphaltene fractions have been investigated in this work. Correlations were derived which show that the vacuum residual oil bulk properties density, Conradson carbon content, and viscosity correlate with residual oil hydrogen content, H/C atomic ratio, the fraction of aromatic carbon, saturate, and asphaltene content. It was found that the VRO metal (Ni + V) content was almost evenly distributed between the maltene and the asphaltene fractions. The data in this work presented contradictory facts about the molecular weight of the VRO asphaltene fractions. The simulation distillation data (ASTM D-7169) and Goosens' correlation support the statement of Mullins et al. that the asphaltene fractions may have molecular weight of about 750 g/mole. The atmospheric residue physical distillation data (ASTM D-5236) and Riazi's boiling point distribution model, however support the statement that the asphaltenes are concentrated in the higher boiling point, higher molecular weight VRO fractions. The higher the aromaticity of a heavy oil, the higher its viscosity is. Since the asphaltenes are the most aromatic compounds in a heavy oil their influence on the heavy oil viscosity is the biggest among all other heavy oil constituents. The converted vacuum residual oils (from visbreaking and residue ebullated bed H-Oil hydrocracking) demonstrated lower dependence of viscosity on the asphaltene content. This could be a result from decreasing of the dimensions of the macro-structure of the converted asphaltene molecule.

23. Effect of commercially available antioxidants over biodiesel/diesel blends stability

The main obstacle in biodiesel/conventional diesel blends acceptance worldwide seems to be its poor oxidative stability. Low resistance towards oxygenation is due to the fatty constituent in the blend. Even low concentrations of biodiesel (5%, 10% and 20%) can contribute to sticky, viscous and polymeric deposits formation after several months of storage. Two correlations were derived concerning insolubles formed in both stabilized and not stabilized blends, stressed under conditions of ASTM D2274. For treated with antioxidant additive:

$$\text{Total insol.} = 0.6561 + 80.1213 * \Delta\text{TAN} - 2.6073 * \Delta\text{IV}$$

For not stabilized samples:

$$\text{Total insol:} = -229.348338 - 13.2360978 * \Delta\text{TAN} + 968.531862 * \Delta\text{Visc} - 25.0335999 * \Delta\text{IV}$$

	<p>The correlations' precision is described by the high value of $R^2 = 1.0000$.</p> <p>Present work proves that it is possible to stabilize such a blend even the fatty component is aged for a period of three months.</p>
24	<p style="text-align: center;">Challenges in characterization of residual oils. A review</p>
	<p>This paper passes over the literature for residual oil characterization. The methods for residual oil characterization are classified in: characterization based on physical and chemical bulk properties; characterization based on saturates, aromatics, resins, asphaltenes (SARA) analysis; and characterization based on the molecular modeling processes. The upper and lower limits of the values for physical and chemical bulk properties of the vacuum residual oils around the world are outlined. A variation of the physical and chemical bulk properties of SARA fractions originating from different vacuum residual oils is discussed. Correlations between refractive index and density, and between the vapor pressure osmometry (VPO) molecular weight of saturates and aromatics were found. A ratio between the lowest and the highest molecular weight of the vacuum residual oil saturate and aromatic fraction of 2.4 was found showing that the molecular weights of these SARA fractions are not fixed and can vary between 360 and 880 g/mole for the saturates, and 450 and 1080 g/mole for the aromatics. Assuming the same ratio in variation of molecular weights (MW) of the fractions resins and asphaltenes for the reviewed 41 vacuum residual oils suggests that the resins MW could vary in the range 800÷1800 g/mole and the asphaltenes MW may vary between 1000 and 3000 g/mole. The application of sophisticated analytical techniques showed a very big diversity in the species building the vacuum residual oils and different distribution of these species even for the same SARA fraction depending on the residual oil origin. The different approaches for “molecular reconstruction” of residual oils Monte Carlo (MC), Quadrature algorithm (QA), Entropy maximization (EM), quantitative structure-property relationship (QSPR), structure-oriented lumping (SOL), molecular type homologous series (MTHS) matrix, artificial neural network (ANN) and multiple linear regression (MLR) are reviewed. A conclusion is made that the advanced analytical and computational techniques are still an obligor to the chemical engineers working at the commercial residual oil conversion units who aim to optimize the conversion process performance.</p>
25.	<p style="text-align: center;">Variation of oxidation reactivity of straight run and H-Oil hydrocracked vacuum residual oils in the process of road asphalt production</p>
	<p>Four straight run vacuum residual oils (SRVRO) and five H-Oil hydrocracked vacuum residual oils (H-Oil VTB) and their blends were oxidized in a laboratory autoclave reactor. It was found that the addition of H-Oil VTB to the SRVRO increases the oxidation rate of the SRVRO, which leads to a higher rate of asphaltenes formation, and subsequently higher rate of softening point increasing. The oxidation rate expressed by the rate of softening point increasing with oxidation time prolonging of the blends SRVRO/H-Oil VTB linearly</p>

correlates with the colloidal instability index (CII) of the H-Oil VTB. The oxidation rate of the SRVRO was also found to correlate with the CII of the SRVRO. Inhibiting the oxidation process for the road asphalt containing H-Oil VTB by improvement the colloidal stability and compatibility of the blend can allow increasing the share of the H-Oil VTB in the feed for production of road asphalt.

26. **Feasibility of Bitumen Production from Unconverted Vacuum Tower Bottom from H-Oil Ebullated Bed Residue Hydrocracking**

In relation to the constant requirement for reduction of sulfur level and low demand for fuel oil, this study presents an approach for utilization of unconverted vacuum tower bottom (UVTB) from the ebullated bed hydrocracking process, H-Oil technology, in bitumen production. The kinetic study shows a slower softening point increase for crude blend 70% Urals and 30% Middle Eastern than other feeds in the air-blowing process. Also, penetration values for straight run vacuum residue feeds decrease quicker than the increase in their softening point values. UVTB softening point increase at high temperature is faster and penetration decrease is slower than LNB SRVR. Air blowing is shown to improve the penetration index of UVTB to a greater extent than the SRVR one. The bottleneck of this new application of UVTB is its low resistance to hardening, determined by using a rolling thin film oven (RTFO), which limits its quantity up to 20–30% in blends.

27. **Effect of catalyst condition on sedimentation and conversion in the ebullated bed vacuum residue H-Oil hydrocracking**

This study highlights the importance of the condition of the catalytic system in the ebullated bed vacuum residue hydrocracker on the performance of the unit, proving that not only feedstock quality but also catalytic system quality are the single variables which have the biggest impact on residue hydrocracker performance. During processing the same vacuum residual oil in the LUKOIL Neftohim Burgas H-Oil ebullated bed hydrocracker a variation of conversion between 56.6 and 73.0% was observed. A higher sedimentation and the resulted decreased reaction severity were provoked by a higher vanadium content in the catalyst in the second reactor and a higher arsenic determinant in the whole catalytic system. The reduction of the second reactor catalyst vanadium content along with a decrease of the arsenic determinant in the whole catalytic system allowed recovering the 16.4% loss of conversion during processing the same feedstock. The increase of reaction temperature at constant liquid hourly space velocity (LHSV) increases aromaticity of the unconverted vacuum residual oil product, most probably due to dealkylation of the side alkyl groups attached to the aromatic cores. The raise of temperature also had an effect on the increase of asphaltene conversion, a fact that is not always observed during EBRHC of vacuum residual oils from different origin.

28.	<p align="center">Impact of H-Oil vacuum residue hydrocracking severity on fluid catalytic cracking unit performance</p>
<p>The performance of both ebullated bed H-Oil vacuum residue (VR) hydrocracking and fluid catalytic cracking (FCC) of vacuum gas oils (VGO) is interrelated. The increase of H-Oil unit reaction temperature maximizes VR conversion and augments the aromaticity and density of the hydrocracked heavy oils. The FCC of VGO blends that contain more aromatic H-Oil VGOs is featured by a lower VGO conversion. It was found in this study that the reactivity of the H-Oil heavy oils depends on their molecular weight (T50) instead on their aromatics content as observed during catalytic cracking of straight run VGOs reported in other studies.</p>	
29.	<p align="center">Dependence of Fluid Catalytic Cracking Unit Performance on H-Oil Severity, Catalyst Activity, and Coke Selectivity</p>
<p>The effect of the quality of ebullated bed vacuum residue H-Oil hydrocracking gas oils cracked in a commercial fluid catalytic cracking unit (FCCU) on its performance was studied. Six different catalysts were employed in this study. Four catalysts were tested in a commercial FCCU, and two in a laboratory FCCU. An increase of the H-Oil hydrocracker reaction temperature was associated with a decrease in the Kw factor of the H-Oil gas oils. The diminished Kw factor of H-Oil gas oils resulted in lower FCCU conversion and higher regenerator temperatures. The FCC conversion at maximum gasoline yield is best predicted by the feed Kw factor. The higher-activity, higher Δ coke catalyst is unfavorable for FCCU performance because the excessive regenerator temperature excursions require reduction of the throughput.</p>	
30.	<p align="center">Investigation on feasibility to simulate distribution of boiling point and molecular weight of heavy oils</p>
<p>Thirty-four heavy oils originating from the four main groups of crude oils around the world—I group: light, low sulfur (30–40⁰ API; S \leq 0.5% mass); II group: light sulfur (30–40⁰ API; S = 0, 5–1.5% mass); III group: heavy, high sulfur (15–30⁰ API; S = 1.5, 3.1% mass); IV group: extra heavy, high sulfur (15⁰ API, S \geq 3% mass)—were investigated for distribution of boiling point and molecular weight. The three-parameter distribution model of Riazi and the four-parameter Weibull extreme distribution function were tested to approximate the distribution of the heavy oil properties mentioned. It was found that the Weibull extreme more accurately approximates the heavy oil boiling point distribution up to temperatures of 750 °C, and molecular weight distribution up to 955 g/mol. To approximate distribution of higher values extrapolation is needed. Riazi's distribution model was found to be more precise in the</p>	

extrapolation than the Weibull extreme.

31. **Impact of feed properties on gasoline olefin content in the fluid catalytic cracking**

Eight vacuum gas oils (VGOs) having different hydrocarbon composition and different distillation characteristics were cracked in a laboratory fluid catalytic cracking (FCC) advanced cracking equipment (ACE) unit. The experimental results showed that FCC VGO feedstock reactivity correlates with the content of saturates plus light aromatics, and with the content of nitrogen. The FCC gasoline olefin content was found to depend on T50% and saturate content of the FCC VGO feedstock. The results from a commercial FCC unit that processes a hydrotreated straight-run VGO and a VGO from ebullated bed residue H-Oil hydrocracker confirmed the results from the laboratory FCC ACE unit showing that reducing T50% and increasing saturate content of the FCC feedstock leads to a reduction of the FCC gasoline olefin content.

32. **Relationship of the aromatic structural types in vacuum gas oil to empirical correlations based on bulk properties**

Five empirical methods to estimate the content of aromatic, naphthenic, and paraffinic carbon and hydrogen content and the bulk properties were tested for prediction of aromatic structures content of 95 vacuum gas oils. The density demonstrated the highest correlation with the aromatic structures content among all other studied bulk properties and empirical parameters. The aromatic structures content could be predicted by a second order power law dependence on density with accuracy commensurable with the reproducibility of SARA analysis. The poly-nuclear aromatic structures content was also found to depend on the density and can be expressed by a linear function.

33. **Physical Vacuum Distillation and High Temperature Simulated Distillation of Residual Oils from Different Origin**

High temperature simulated distillation (HTSD) of residual oils is not only faster but also more precise than the physical vacuum distillation (ASTM D-5236). However, the HTSD ASTM D-7169 method could report wrong results if it is not performed properly. A verification of the correctness of the HTSD analysis could be accomplished by comparison of the HTSD curve with the one of the physical vacuum distillation methods (ASTM D-1160 or ASTM D-5236). The calibration blend, design of the liner, the GC inlet temperature, and the concentration of heavy oil sample in CS₂ were found to have a considerable impact on the correctness of the reported results. The conversion of HTSD in ASTM D-5236 developed in this work is able to predict the distillation curve of the ASTM D-5236 vacuum distillation

with almost the same precision as its repeatability of the method.

34. **Investigation of the fluid catalytic cracking of different H-Oil vacuum gas oils and their blends with hydrotreated vacuum gas oil**

H-Oil vacuum gas oils obtained during hydrocracking of vacuum residual oils originated from the crudes Russian Export Blend, Basrah light, and Heavy Kazakh were cracked in a mixture with a hydrotreated vacuum gas oil in the LUKOIL Neftohim Burgas commercial fluid catalytic cracking (FCC) unit. Some of the H-Oil vacuum gas oils were also cracked in a laboratory FCC (ACE) unit. The results from the commercial and the laboratory tests showed that the laboratory FCC experiments in an ACE unit can be used to evaluate the effect of feed quality on the commercial FCC unit performance. The assumption that the conversion of a vacuum gas oil (VGO) blend in the fluid catalytic cracking could be considered as a linear combination of the conversion of the individual components made by other researchers was also confirmed in this study. The higher the hydrogen content in the vacuum residual oil of a crude is the higher the FCC conversion of the H-Oil VGO, obtained during hydrocracking of that high saturate vacuum residual oil, will be expected.

35. **Colloidal stability and hot filtration test of residual fuel oils based on visbreaking and ebullated bed residue H-Oil hydrocracking**

Six H-Oil-based residual fuel oils, two H-Oil atmospheric tower bottom products, two H-Oil vacuum tower bottom products, one visbreaker-based residual fuel oil, and three different straight run vacuum residual oils were studied in this work. The colloidal stability parameters S-value (ASTM D7157), and separability number (ASTM D7061), along with SARA-based colloidal instability index, and the solubility parameters of asphaltene and maltene fractions of the studied residual oils were tested to correlate with the residual oil sediment content. It was found that none of the colloidal stability parameters correlated with the residual oil sediment content, while correlations were found between the different colloidal stability parameters. This study has shown that only the residual oil samples whose S-value has been at minimum of 1.375 kept their sediment contents without change with the course of time.

36. **Evaluation of accuracy of available in literature gasoline blending models to predict octane numbers of gasoline blends**

The gasoline blending prediction models available in the open literature: Linear method, Ethyl method, Stewart method, Zahed method, and Twu method were tested on 25 gasoline blends prepared from 14 components used by LUKOIL Neftohim Burgas (LNB) refinery to produce commercial gasoline grades. The performed tests with these models showed

prediction accuracy outside of the acceptable ASTM D 2699 and ASTM D 2700 reproducibility limits. However, the LNB-modified regression model of Zahed method turned out to predict RON and MON of studied gasoline blends with accuracy equivalent to the reproducibility of the standard methods for measurement of RON and MON.

37. **Laboratory and commercial investigation of ebullated bed residue hydrocracking performance during processing of Urals crude vacuum resid and its blends with vacuum gas oil and atmospheric residue**

This study focuses on investigating the conversion behaviour of vacuum residue and blends with heavy VGO (480–540 °C) and atmospheric residue (340°C+), three fractions originating from the same Russian export blend crude oil (REBCO), in a laboratory ebullated bed hydrocracking pilot plant unit and in the LUKOIL Neftohim Burgas commercial H-Oil_{RC} hydrocracker. It was found that the vacuum residue conversion was 1.7 times as high as that of the VGO at the same operating conditions in both laboratory and in the commercial H-Oil_{RC} hydrocracking unit. No increase in the sediment content of the atmospheric residue product, obtained during hydrocracking of the lighter feeds, was observed. It was found that the vacuum residue H-Oil hydrocracking is best described by 1.5 order kinetics. This study showed that co-processing of distillate material (mainly vacuum gas oil) is an option to increase capacity of an existing H-Oil_{RC} residue hydrocracker while also improving the VGO product quality without adversely impacting sediment levels in the unconverted residue product.

38. **Feed properties effect on the performance of vacuum residue ebullated bed H-Oil hydrocracking**

24 vacuum residual oils originating from 15 crudes and three imported atmospheric residual oils were processed in the LUKOIL Neftohim Burgas (LNB) ebullated bed vacuum residue (EBVR) H-Oil hydrocracking unit. During their processing the sediments content in the atmospheric tower bottom (ATB) product, that correlates with the rate of fouling of the H-Oil equipment, was kept at approximately 0.4%. At this level of sediments in the ATB product the conversion was found to increase with the feed colloidal instability index (CII) reduction and asphaltene conversion enhancement. It was found that asphaltenes from the feed 100% Urals VR participate more readily in recombination reactions in comparison with the asphaltenes coming from crudes from Middle East. This leads to a decrease in the value of asphaltene conversion and to an increase of sedimentation. The reduction of feed CII and improvement of asphaltene conversion allows an increase in the hydrocracking reaction severity, resulting in a higher VR conversion and higher yields of higher value products at the expense of the lower yield of the lower value VTB product.

39.

About H-Oil performance improvement and cetane number of finished refinery diesel

It was observed in the LUKOIL Neftohim Burgas refinery that the employed 2-ethyl hexil nitrate cetane improver treating rate increased by a factor of two for the last 17 months. An analysis performed using intercriteria analysis revealed that the main culprit for cetane improver treating rate augmentation is the deterioration of the cetane index of the finished automotive diesel fuel as a result of the increased H-Oil severity of operation. The estimation of the cetane number (index) of the refinery diesel fuel employing the linear blending rule established that the high severity mode of operation of H-Oil leads to production of refinery diesel having about 1 point lower cetane index (number). The slope of enhancement of diesel fuel with magnification of cetane improver treating rate indicated that 1 point lower diesel cetane number (index) will need about 370 ppm higher cetane improver treating rate.

40. What Is Behind the High Values of Hot Filtration Test of the Ebullated Bed Residue H-Oil Hydrocracker Residual Oils?

This work summarizes the results of multiple experiments performed in the LUKOIL Neftohim Burgas Research Laboratory related to the issue of high values of hot filtration test (HFT) of the residue H-Oil hydrocracking residual oil products. After the start-up of the new residue H-Oil hydrocracker in the LUKOIL Neftohim Burgas refinery during the second half of 2015 the values of the HFT of the vacuum tower bottom product varied between 0.01 and 8.7%. It was found that the vacuum residual oil feed source has a profound effect on the processes of sedimentation in the H-Oil hydrocracker. The processing of vacuum residual oils from Arab medium, Arab heavy, and Basrah light crudes reduced the sedimentation and allowed achievement of a higher conversion. The H/C ratios of asphaltenes from all studied feeds decreased after hydrocracking. However, the decrease of the H/C ratio was the least pronounced with the Basra light asphaltenes, while the H/C ratios of asphaltenes from the vacuum residual oils originating from the crudes Urals and El Bouri became much lower. The maltene fraction H/C ratio could become lower, the same, or higher after hydrocracking depending on the feed source, catalyst metal (vanadium) loading, or the hydrocracking unit (commercial, pilot plant, or laboratory unit). It was found that after addition of high aromatic fluid catalytic cracking gas oils the H-Oil residue HFT dropped and the dependence of the residue HFT on the concentration of FCC gas oils in the blend could be approximated by a third order polynomial. Correlations were developed to predict the H-Oil based residual fuel oil HFT from information on the base H-Oil residue HFT and the amount of added fluid catalytic cracking (FCC) gas oil. The treatment of the H-Oil residual oils with commercial HFT reducers may decrease the residual oil HFT. However, the efficiency in HFT reduction turned out to depend on the nature of the H-Oil residue and on the concentration range of the HFT reducing additive. From all studied additives solely the dodecylbenzenesulfonic acid (DBSA) was capable of reducing the H-Oil residual oil below 0.1%. However, the treatment rate of the DBSA was an order higher than that of the commercial additives A, B, and C. DBSA was an order of magnitude more effective in the reduction of the total sediment

existent, and the total sediment potential than the FCC HCO.

41. Impact of oil compatibility on quality of produced fuel oil during start-up operations of the new residue ebullated bed H-Oil hydrocracking unit in the LUKOIL Neftohim Burgas refinery

During start-up operations of the new residue ebullated bed H-Oil hydrocracking unit in the LUKOIL Neftohim Burgas refinery oil incompatibility was registered in the process of production of heavy fuel oil. That was the reason for obtaining high sediment off-spec heavy fuel oil product. The oil incompatibility was observed in the process of blending of high saturate, low asphaltene, high colloidal stability H-Oil unconverted vacuum residue with the high aromatic, and relatively high asphaltene visbroken residue. The use of antifouling additive was found to decrease the sediment level in the heavy fuel oil. However, it was not capable of reducing the heavy fuel oil sediment content after chemical and thermal artificial aging of the fuel oil. Considerable amount of high aromatic fluid catalytic cracking heavy cycle oil was needed to reduce the off-spec heavy fuel oil sediment content to the specified max. limit of 0.1% sediments. After deasphaltization of the visbroken residue with n-heptane and blending of the visbroken deasphalted oil with the H-Oil unconverted vacuum residue in a ratio of 1:1 the sediment content of the heavy fuel oil blend dropped from 2.5% to 0.01%. This suggests that the lower solubility of the visbroken residue asphaltenes in the high saturate H-Oil unconverted vacuum residue was the reason for the oil incompatibility during the production of off-spec heavy fuel oil in the LUKOIL Neftohim Burgas refinery when both the H-Oil residue hydrocracker and the visbreaker were in operation.